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| <p>(54) Title: COPPER CHEMICAL-MECHANICAL POLISHING PROCESS USING A FIXED ABRASIVE POLISHING PAD AND A COPPER LAYER CHEMICAL-MECHANICAL POLISHING SOLUTION SPECIFICALLY ADAPTED FOR CHEMICAL-MECHANICAL POLISHING WITH A FIXED ABRASIVE PAD</p> <div data-bbox="511 1113 1144 1522"> </div> <p>(57) Abstract</p> <p>The invention comprises copper chemical-mechanical polishing processes using fixed abrasive polishing pads, and copper layer chemical-mechanical polishing solutions specifically adapted for chemical-mechanical polishing with fixed abrasive pads. In one implementation, processes are described for pH's of 7.0 or greater. In one implementation, processes are described for pH's of 7.0 or less. In one implementation, a copper layer chemical-mechanical polishing solution specifically adapted for chemical-mechanical polishing with a fixed abrasive pad comprises a copper oxidizing component present at from about 1 % to 15 % by volume, a copper corrosion inhibitor present at from about 0.01 % to 2 % by weight, and a pH of less than or equal to 7.0. In one implementation, a copper layer chemical-mechanical polishing solution specifically adapted for chemical-mechanical polishing with a fixed abrasive pad comprises a copper oxidizing component present at from about 0.1 % to 15 % by volume, a copper complexing agent present at from about 0.1 % to 15 % by volume, and a pH of greater than or equal to 7.0.</p> | | |

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DESCRIPTION

COPPER CHEMICAL-MECHANICAL POLISHING PROCESS USING A FIXED ABRASIVE POLISHING PAD AND A COPPER LAYER CHEMICAL-MECHANICAL POLISHING SOLUTION SPECIFICALLY ADAPTED FOR 5 CHEMICAL-MECHANICAL POLISHING WITH A FIXED ABRASIVE PAD

Technical Field

This invention relates to copper chemical-mechanical polishing processes using fixed abrasive polishing pads, and to copper layer chemical-mechanical
10 polishing solutions specifically adapted for chemical-mechanical polishing with fixed abrasive pads.

Background Art

In the manufacture of integrated circuits from semiconductor wafers and substrates, wafer polishing is a common technique utilized to remove material
15 and/or achieve planarity. Such polishing can be conducted by purely chemical, purely mechanical or chemical-mechanical polishing means (CMP). With CMP, polishing and removal occurs by a combination of both chemical and mechanical polishing action. CMP utilizes a combination of solid abrasives and chemicals to achieve the combination polishing action. One type of chemical-mechanical
20 polishing utilizes a slurry comprising very hard, solid abrasive particles suspended in a chemical solution. The slurry is interposed between a pad and a wafer, with both typically being caused to rotate, and material removed from the wafer by both chemical and mechanical action. Another form of CMP provides abrasive material embedded within the surface of the polishing pad, and is
25 commonly referred to as fixed abrasive CMP.

Unfortunately, conventional CMP slurries designed for non-fixed abrasive CMP create problems and do not always work satisfactorily in fixed abrasive CMP processes. This has been discovered to be particularly true in the CMP of layers where copper is present at greater than or equal to fifty atomic
30 percent. Increasing interest is being focused on copper as a next generation material for interconnect lines in semiconductor circuitry fabrication. CMP of copper in processes of forming such lines will play a significant and valuable role in the fabrication of such circuitry. While CMP of copper has been reported using non-fixed abrasive pads and slurries, existing materials have proven less than
35 satisfactory when using fixed abrasive pads. Accordingly, needs remain for

improved chemical-mechanical processes using fixed abrasive pads and in the development of polishing solutions therefor.

Brief Description of the Drawings

Fig. 1 is a diagrammatic view of a prior art chemical-mechanical polishing apparatus used in accordance with an aspect of the invention.

Best Modes for Carrying Out the Invention and Disclosure of Invention

The invention comprises copper chemical-mechanical polishing processes using fixed abrasive polishing pads, and copper layer chemical-mechanical polishing solutions specifically adapted for chemical-mechanical polishing with fixed abrasive pads. In the context of this document unless otherwise specifically literally narrowed, a "copper layer" constitutes a layer having copper present at least at 50% molar. In one implementation, processes are described for pH's of 7.0 or greater. In one implementation, processes are described for pH's of 7.0 or less. Believed process mechanisms by which polishings occur in accordance with the invention are disclosed, but are not intended to be limiting unless expressly worded in the respective claim.

In one implementation, a copper layer chemical-mechanical polishing solution specifically adapted for chemical-mechanical polishing with a fixed abrasive pad comprises a copper oxidizing component present at from about 1% to 15% by volume, a copper corrosion inhibitor present at from about 0.01% to 2% by weight, and a pH of less than or equal to 7.0. In one implementation, a copper layer chemical-mechanical polishing solution specifically adapted for chemical-mechanical polishing with a fixed abrasive pad comprises a copper oxidizing component present at from about 0.1% to 15% by volume, a copper complexing agent present at from about 0.1% to 15% by volume, and a pH of greater than or equal to 7.0.

In accordance with one aspect of the invention, a semiconductor wafer having an outer layer or region comprising copper at greater than or equal to 50% molar is polished with improved solutions using fixed abrasive pads. The invention was principally predicated upon the chemical-mechanical polishing of copper layers consisting essentially of elemental copper. However, the invention is anticipated to have applicability to polishing any copper layers having greater than or equal to 50% molar copper content, including such layers consisting essentially of copper alloys.

A wafer having such a layer is positioned within a suitable chemical-mechanical polishing apparatus comprising a fixed abrasive

chemical-mechanical polishing pad. Any suitable apparatus is usable, such as by way of example only, those apparatus which rotate/revolve both a fixed abrasive pad and the wafer, those apparatus which rotate/move a fixed abrasive pad and not the wafer, those apparatus which rotate/revolve the wafer and not a fixed
5 abrasive pad, etc. Fixed abrasive pads can be purchased from many suppliers, such as the 3M Company of St. Paul, Minnesota, U.S.A. A copper layer chemical-mechanical polishing solution in accordance with the invention is provided intermediate the pad and the wafer utilizing the polishing equipment. In one implantation, the solution comprises a copper oxidizing component present
10 at from about 0.5% to 15% by volume, a copper corrosion inhibitor present at from about 0.01% to 2% by weight, and a solution pH of less than or equal to 7.0.

Example preferred oxidizing components include ammonium compounds and nitrate compounds. Specific examples include ferric nitrate, hydrogen peroxide,
15 ammonium persulfate, ammonium molybdate, nitric acid, potassium iodate, potassium nitrate and mixtures thereof. Example preferred copper corrosion inhibitors include azoles such as benzotriazole, mercaptabenzothiazole and tolytriazole; amines such as methylamine and diethylamine; ring compounds such as pyridine, quinoline, and dicyclohexamine nitrite; other compounds such as
20 potassium silicate, ammonium borate, ammonium phosphate and potassium dichromate; and mixtures thereof. A solution pH is more preferably kept at less than 5.0, with the solution also preferably comprising a pH buffer at, for example, 0.1% to 10% by weight. Example buffers include potassium hydrogen phthalate, ammonium phosphate, ammonium acetate, ammonium dihydrogen
25 phosphate, dibasic ammonium citrate, ammonium hydrogen phosphate, tribasic ammonium citrate, ammonium oxalate, ammonium carbamate and mixtures thereof.

The solution can also comprise a surfactant, for example present at a concentration of from 1% to 10% by volume. Example surfactants include polyethylene glycol, polyoxyethylene ether, glycerol, polypropylene glycol,
30 polyoxyethylene lauryl ether, polyoxyethylene cetyl ether, polyoxyethylene stearyl ether, polyoxyethylene oleyl ether, and mixtures thereof. The solution might further comprise thickeners to achieve desired viscosity, with an example preferred range being from about 10 centipoise to 20 centipoise at room temperature. Examples of thickeners include PolyoxTM available from Union Carbide of
35 Danbury, Connecticut U.S.A., and CarbopolTM available from B.F. Goodrich of Cleveland, Ohio U.S.A.

The solution is most ideally provided to be void of solid abrasive material, at least prior to starting chemical-mechanical polishing. Once polishing commences with the fixed abrasive pad, it is possible that some abrasive material from the pad will break off of the pad and find its way into solution, but
5 ideally the solution is essentially abrasive-free in accordance with the most preferred aspects of the invention.

With such exemplary solutions in accordance with the invention received intermediate the wafer and pad, the copper comprising layer is chemical-mechanical polished with the fixed abrasive pad.

10 In another considered aspect of the invention, copper from the layer being polished is oxidized with a solution comprising a copper corrosion inhibitor present at from about 0.01% to 2% by weight, and having a pH of less than or equal to 7.0. One or both of copper and copper oxide from the copper comprising layer is polished with a fixed abrasive chemical-mechanical polishing
15 pad. The oxidized copper might oxidize on the layer prior to removal, or be polished/etched away from the layer as copper and be oxidized and dissolved in solution thereafter. Both of these actions might also occur, with one or the other possibly predominating. Solution components during polishing preferably constitute those as described above, and again in significant consideration is
20 ideally void of solid abrasive material. Polishing preferably is conducted at atmospheric pressure and anywhere from 40°F up to 145°F, although other conditions are of course possible.

In an alternate aspect of the invention, a chemical-mechanical polishing process and solution therefor comprises a copper oxidizing component present at
25 from 0.1% to 15% by volume, a copper complexing agent present at from about 0.1% to 15% by volume, and a pH of greater than or equal to 7.0. Some exemplary copper oxidizing components in accordance with this aspect include those as described above. A preferred complexing agent comprises ammonia. Such can be, for example, derived from a material in the solution selected from
30 the group consisting of ammonium hydroxide, diammonium hydrogen phosphate, ammonium dihydrogen phosphate, ammonium acetate, tribasic ammonium citrate, dibasic ammonium citrate, ammonium oxalate, ammonium carbamate and mixtures thereof. The solution most preferably comprises a pH of less than or equal to 10.0, and also includes a pH buffer which in some cases can be the same as
35 the complexing agent. For example, each of ammonium hydroxide, diammonium hydrogen phosphate, ammonium dihydrogen phosphate, ammonium acetate, tribasic

ammonium citrate, dibasic ammonium citrate, ammonium oxalate and ammonium carbamate can also provide a pH buffering function. Surfactants, thickeners and copper corrosion inhibitors can and are preferably utilized where appropriate, as described above.

5 In another considered aspect of the invention, copper is polished from a layer comprising copper at greater than or equal to 50% molar using a fixed abrasive chemical-mechanical polishing pad. During the polishing, at least one of Cu^{++} and Cu^+ from the copper layer is provided into a solution comprising ammonia and a pH greater than or equal to 7.0. The Cu^{++} and/or Cu^+ is
10 complexed with the ammonia in that solution. More specifically, during polishing oxidizers help in conversion of Cu to $\text{Cu}^+/\text{Cu}^{++}$ either by oxidizing copper on the layer surface and/or by converting Cu to $\text{Cu}^+/\text{Cu}^{++}$ once copper is abraded and is in the solution. Once copper ions are in the solution, ammonium based compounds in the solution complex the ions. Again most preferably, the solution
15 is void of solid abrasive material, at least prior to starting said polishing.

Example slurry abrasives of the prior art in the chemical mechanical polishing of copper include SiO_2 , CeO_2 and Al_2O_3 . In certain desired polishing actions, one might be more favored than another. Further, different pH ranges using the different abrasives might be desired for each abrasives. Yet in prior
20 art chemical-mechanical polishing solutions and process, it has been found that the abrasives do not remain well dispersed throughout the solution at certain desired pH's. For example, SiO_2 will not stay well dispersed in solution if pH falls below 4. CeO_2 will not stay well dispersed in solution at a neutral pH around 7. Al_2O_3 will not stay well dispersed in solution if pH rises too high.
25 This has typically resulted in using a less desirable abrasive for a given application where a specific pH is desired. Yet fixed abrasive polishing using solutions of the invention in combination with using a fixed abrasive pad can enable utilization of desired abrasives across a wider pH range.

Further in many instances, it would be desirable to maintain temperature
30 at or below room temperature during the copper polish (i.e., at or below 74°F). This is seldom practical where lower slurry temperature will also result in poor abrasive material dispersal throughout the slurry during polish. Accordingly, elevated temperatures are utilized during the polish. Yet in accordance with an aspect of the invention, slurry temperature during polish can be maintained at
35 or below room temperature (further preferably at or below 65°F) where the abrasive is fixed on the pad and agglomeration of abrasives within the slurry is

not a concern. Polishing in all embodiments preferably is conducted at atmospheric pressure and anywhere from 40°F up to 145°F, although other conditions are of course possible.

Example equipment and processing utilized in accordance with the invention is described with reference to Fig. 1, wherein a web-format planarizing machine 10 is used for chemical-mechanical polishing a semiconductor wafer 12. Planarizing machine 10 has a support table 14 with a top panel 16 at a work station where an operative portion (A) of a planarizing pad 40 is positioned. The top-half panel 16 is generally a rigid plate to provide a flat, solid surface to which a particular section of planarizing pad 40 may be secured during polishing.

Planarizing machine 10 also has a plurality of rollers to guide, position and hold planarizing pad 40 over top panel 16. The rollers include a supply roller 20, first and second idler rollers 21a and 21b, first and second guide rollers 22a and 22b, and a take-up roller 23. The supply roller 20 carries an unused or pre-operative portion of the planarizing pad 40, and take-up roller carries a used or post-operative portion of planarizing pad 40. First idler roller 21a and first guide roller 22a stretch planarizing pad 40 over top panel 16 to hold the planarizing pad 40 stationary during operation. Planarizing pad 40 in accordance with the invention preferably comprises a fixed abrasive pad, such as described above, and having a length greater than a maximum diameter of the wafers being polished. A motor (not shown) drives at least one of supply roller 20 and take-up roller 23 to sequentially advance the planarizing pad 40 across the top-panel 16. As such, clean pre-operative sections of the planarizing pad 40 may be quickly substituted for used sections to provide a consistent surface for planarizing and/or cleaning the substrate.

The web-format planarizing machine 10 has a carrier assembly 30 that controls and protects wafer 12 during polishing. Carrier assembly 30 generally has a substrate holder 32 to pick up, hold and release wafer 12 at appropriate stages of the polishing cycle. A plurality of nozzles 33 attached to substrate holder 32 dispense a planarizing solution 44 in accordance with the invention onto a planarizing surface 42 of planarizing pad 40. Carrier assembly 30 also generally has a support gantry 34 carrying a drive assembly 35 that translates along gantry 34. Drive assembly 35 generally has an actuator 36, a drive shaft 37 coupled to the actuator 36, and an arm 38 projecting from drive shaft 37. Arm 38 carries substrate holder 32 via another shaft 39 such that

drive assembly 35 orbits substrate holder 32 about an axis B-B offset from a center point C-C of wafer 12.

In accordance with an aspect of the invention, the process preferably comprises moving web/pad 40 a distance less than the maximum diameter of the
5 wafer such that a subsequently polished wafer is exposed to a fresh pad segment which was not utilized to polish the immediately preceding wafer. Preferably, the distance moved is less than or equal to 1.0% of the maximum diameter for uniformity of polish and to extend life of the pad. For example for an 8-inch diameter wafer, an incremental movement of pad/web 40 between each polishing
10 is 0.25 inch.

CLAIMS

1. A chemical-mechanical polishing process comprising:
providing a semiconductor wafer having a layer comprising copper at least
at 50% molar;
5 positioning the wafer in proximity with a fixed abrasive chemical-mechanical
polishing pad;
providing a copper layer chemical-mechanical polishing solution intermediate
the wafer and pad, the copper layer chemical-mechanical polishing solution
comprising a copper oxidizing component present at from about 0.5% to 15%
10 by volume, a copper corrosion inhibitor present at from about 0.01% to 2% by
weight, and a pH of less than or equal to 7.0; and
chemical-mechanical polishing the copper comprising layer with the fixed
abrasive pad with the copper layer chemical-mechanical polishing solution being
received between the wafer and pad.
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2. The chemical-mechanical polishing process of claim 1 wherein the
layer consists essentially of elemental copper.
3. The chemical-mechanical polishing process of claim 1 wherein the
20 layer consists essentially of a copper alloy.
4. The chemical-mechanical polishing process of claim 1 wherein the
oxidizer comprises an ammonium compound.
- 25 5. The chemical-mechanical polishing process of claim 1 wherein the
oxidizer comprises a nitrate compound.
6. The chemical-mechanical polishing process of claim 1 wherein the
oxidizer compound is selected from the group consisting of ferric nitrate,
30 hydrogen peroxide, ammonium persulfate, ammonium molybdate, nitric acid,
potassium iodate, potassium nitrate and mixtures thereof.

7. The chemical-mechanical polishing process of claim 1 wherein the inhibitor is selected from the group consisting of benzotriazole, mercaptabenzothiazole, tolytriazole, methylamine, diethylamine, pyridine, quinoline, dicyclohexamine nitrate, potassium silicate, ammonium borate, ammonium
5 phosphate, potassium dichromate and mixtures thereof.

8. The chemical-mechanical polishing process of claim 1 wherein the solution comprises a pH of less than or equal to 5.0.

10 9. The chemical-mechanical polishing process of claim 1 wherein the solution comprises a pH buffer.

10. The chemical-mechanical polishing process of claim 9 wherein the pH buffer is selected from the group consisting of potassium hydrogen phthalate, ammonium phosphate, ammonium acetate, ammonium dihydrogen phosphate, dibasic
15 ammonium citrate, ammonium hydrogen phosphate, tribasic ammonium citrate, ammonium oxalate, ammonium carbamate and mixtures thereof.

11. The chemical-mechanical polishing process of claim 1 wherein the
20 solution comprises a pH of less than or equal to 5.0, and comprises a pH buffer.

12. The chemical-mechanical polishing process of claim 1 wherein the solution comprises a surfactant present at a concentration of from 1% to 10%
25 by volume.

13. The chemical-mechanical polishing process of claim 1 wherein the solution comprises a surfactant selected from group consisting of polyethylene glycol, polyoxyethylene ether, glycerol, polypropylene glycol, polyoxyethylene lauryl
30 ether, polyoxyethylene cetyl ether, polyoxyethylene stearyl ether, polyoxyethylene oleyl ether, and mixtures thereof.

14. The chemical-mechanical polishing process of claim 1 wherein the solution further comprises a thickener and has a viscosity of from about 10
35 centipoise to 20 centipoise at room temperature.

15. The chemical-mechanical polishing process of claim 1 wherein the solution is void of solid abrasive material at least prior to starting said chemical-mechanical polishing.

5 16. The chemical-mechanical polishing process of claim 1 comprising maintaining temperature of the solution during polishing at or below about 74°F.

17. The chemical-mechanical polishing process of claim 1 comprising maintaining temperature of the solution during polishing at or below about 65°F.

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18. The chemical-mechanical polishing process of claim 1 further comprising chemical-mechanical polishing another of said semiconductor wafer in another polishing step using the fixed abrasive pad, the fixed abrasive pad comprising an elongated web of fixed abrasive pad material having a length
15 greater than a maximum diameter of the said wafers being polished, the process comprising moving the web a distance less than the maximum diameter to polish the another wafer with a fresh pad segment not utilized to polish the first polished wafer.

20 19. The chemical-mechanical polishing process of claim 18 wherein the distance is less than or equal to 1.0% of the maximum diameter.

20. A chemical-mechanical polishing process comprising:
providing a semiconductor wafer having a layer comprising copper at least
25 at 50% molar;

oxidizing copper from the layer with a solution comprising a copper corrosion inhibitor present at from about 0.01% to 2% by weight and a pH of less than or equal to 7.0; and

polishing one or both of copper and copper oxide from the copper
30 comprising layer with a fixed abrasive chemical-mechanical polishing pad.

21. The chemical-mechanical polishing process of claim 20 wherein the inhibitor is selected from the group consisting of benzotriazole, mercaptabenzothiazole, tolytriazole, methylamine, diethylamine, pyridine, quinoline,
35 dicyclohexamine nitrate, potassium silicate, ammonium borate, ammonium phosphate, potassium dichromate and mixtures thereof.

22. The chemical-mechanical polishing process of claim 20 wherein the solution comprises a pH of less than or equal to 5.0.

23. The chemical-mechanical polishing process of claim 20 wherein the
5 solution comprises a pH buffer.

24. The chemical-mechanical polishing process of claim 23 wherein the pH buffer is selected from the group consisting of potassium hydrogen phthalate, ammonium phosphate, ammonium acetate, ammonium dihydrogen phosphate, dibasic
10 ammonium citrate, ammonium hydrogen phosphate, tribasic ammonium citrate, ammonium oxalate, ammonium carbamate and mixtures thereof.

25. The chemical-mechanical polishing process of claim 20 wherein the solution comprises a pH of less than or equal to 5.0, and comprises a pH
15 buffer.

26. The chemical-mechanical polishing process of claim 20 wherein the layer consists essentially of elemental copper.

20 27. The chemical-mechanical polishing process of claim 20 wherein the layer consists essentially of a copper alloy.

28. The chemical-mechanical polishing process of claim 20 wherein the polishing is conducted with a solution which is void of solid abrasive material
25 at least prior to starting said polishing.

29. The chemical-mechanical polishing process of claim 20 comprising maintaining temperature of the solution during polishing at or below about 74°F.

30 30. The chemical-mechanical polishing process of claim 20 comprising maintaining temperature of the solution during polishing at or below about 65°F.

31. The chemical-mechanical polishing process of claim 20 further comprising chemical-mechanical polishing another of said semiconductor wafer in another polishing step using the fixed abrasive pad, the fixed abrasive pad comprising an elongated web of fixed abrasive pad material having a length
5 greater than a maximum diameter of the said wafers being polished, the process comprising moving the web a distance less than the maximum diameter to polish the another wafer with a fresh pad segment not utilized to polish the first polished wafer.

10 32. The chemical-mechanical polishing process of claim 31 wherein the distance is less than or equal to 1.0% of the maximum diameter.

33. A copper layer chemical-mechanical polishing solution specifically adapted for chemical-mechanical polishing with a fixed abrasive pad, the solution
15 comprising a copper oxidizing component present at from about 1% to 15% by volume, a copper corrosion inhibitor present at from about 0.01% to 2% by weight, and a pH of less than or equal to 7.0.

34. A chemical-mechanical polishing process comprising:
20 providing a semiconductor wafer having a layer comprising copper at least at 50% molar;

positioning the wafer in proximity with a fixed abrasive chemical-mechanical polishing pad;

providing a copper layer chemical-mechanical polishing solution intermediate
25 the wafer and pad, the copper layer chemical-mechanical polishing solution comprising a copper oxidizing component present at from about 0.1% to 15% by volume, a copper complexing agent present at from about 0.1% to 15% by volume, and a pH of greater than or equal to 7.0; and

chemical-mechanical polishing the copper comprising layer with the fixed
30 abrasive pad with the copper layer chemical-mechanical polishing solution being received between the wafer and pad.

35. The chemical-mechanical polishing process of claim 34 wherein the oxidizing component is selected from the group consisting of ferric nitrate,
35 hydrogen peroxide, ammonium persulfate, ammonium molybdate, nitric acid, potassium iodate, potassium nitrate and mixtures thereof.

36. The chemical-mechanical polishing process of claim 34 wherein the complexing agent comprises ammonia.

37. The chemical-mechanical polishing process of claim 34 wherein the
5 complexing agent comprises ammonia derived from a material in the solution selected from the group consisting of ammonium hydroxide, diammonium hydrogen phosphate, ammonium dihydrogen phosphate, ammonium acetate, tribasic ammonium citrate, dibasic ammonium citrate, ammonium oxalate, ammonium carbamate and mixtures thereof.

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38. The chemical-mechanical polishing process of claim 34 wherein the solution comprises a pH of less than or equal to 10.0.

39. The chemical-mechanical polishing process of claim 34 wherein the
15 solution comprises a pH buffer.

40. The chemical-mechanical polishing process of claim 39 wherein the pH buffer and the complexing agent comprise the same component.

20 41. The chemical-mechanical polishing process of claim 39 wherein the pH buffer is selected from the group consisting of ammonium dihydrogen phosphate, diammonium hydrogen phosphate, ammonium acetate, tribasic ammonium citrate, dibasic ammonium citrate, ammonium oxalate and ammonium carbamate.

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42. The chemical-mechanical polishing process of claim 34 wherein the solution comprises a pH of less than or equal to 10.0, and comprises a pH buffer.

30 43. The chemical-mechanical polishing process of claim 34 wherein the solution comprises a surfactant present at a concentration of from 1% to 10% by volume.

44. The chemical-mechanical polishing process of claim 34 wherein the solution comprises a surfactant selected from group consisting of polyethylene glycol, polyoxyethylene ether, glycerol, polypropylene glycol, polyoxyethylene lauryl ether, polyoxyethylene cetyl ether, polyoxyethylene stearyl ether, polyoxyethylene
5 oleyl ether, and mixtures thereof.

45. The chemical-mechanical polishing process of claim 34 wherein the solution further comprises a thickener and has a viscosity of from about 10 centipoise to 20 centipoise at room temperature.

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46. The chemical-mechanical polishing process of claim 34 wherein the layer consists essentially of elemental copper.

47. The chemical-mechanical polishing process of claim 34 wherein the
15 layer consists essentially of a copper alloy.

48. The chemical-mechanical polishing process of claim 34 wherein the solution is void of solid abrasive material at least prior to starting said chemical-mechanical polishing.

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49. The chemical-mechanical polishing process of claim 34 wherein the solution further comprises a copper corrosion inhibitor.

50. The chemical-mechanical polishing process of claim 49 wherein the
25 inhibitor is selected from the group consisting of benzotriazole, mercaptabenzothiazole, tolytriazole, methylamine, diethylamine, pyridine, quinoline, dicyclohexamine nitrate, potassium silicate, ammonium borate, ammonium phosphate, potassium dichromate and mixtures thereof.

30 51. The chemical-mechanical polishing process of claim 34 comprising maintaining temperature of the solution during polishing at or below about 74°F.

52. The chemical-mechanical polishing process of claim 34 comprising maintaining temperature of the solution during polishing at or below about 65°F.

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53. The chemical-mechanical polishing process of claim 34 further comprising chemical-mechanical polishing another of said semiconductor wafer in another polishing step using the fixed abrasive pad, the fixed abrasive pad comprising an elongated web of fixed abrasive pad material having a length
5 greater than a maximum diameter of the said wafers being polished, the process comprising moving the web a distance less than the maximum diameter to polish the another wafer with a fresh pad segment not utilized to polish the first polished wafer.

10 54. The chemical-mechanical polishing process of claim 53 wherein the distance is less than or equal to 1.0% of the maximum diameter.

55. A chemical-mechanical polishing process comprising:
providing a semiconductor wafer having a layer comprising copper at least
15 at 50% molar;
polishing copper from the copper comprising layer with a fixed abrasive chemical-mechanical polishing pad; and
during the polishing, providing at least one of Cu^{++} and Cu^+ from the copper layer into a solution comprising ammonia and a pH greater than or equal
20 to 7.0, and complexing said at least one of Cu^{++} and Cu^+ with said ammonia in said solution.

56. The chemical-mechanical polishing process of claim 55 wherein the solution comprises both Cu^{++} and Cu^+ .
25

57. The chemical-mechanical polishing process of claim 55 wherein the solution comprises a pH of less than or equal to 10.0.

58. The chemical-mechanical polishing process of claim 55 wherein the
30 solution comprises a pH buffer.

59. The chemical-mechanical polishing process of claim 58 wherein the pH buffer is selected from the group consisting of ammonium dihydrogen phosphate, diammonium hydrogen phosphate, ammonium acetate, tribasic
35 ammonium citrate, dibasic ammonium citrate, ammonium oxalate and ammonium carbamate.

60. The chemical-mechanical polishing process of claim 55 wherein the solution comprises a pH of less than or equal to 10.0, and comprises a pH buffer.

5 61. The chemical-mechanical polishing process of claim 55 wherein the solution comprises a surfactant present at a concentration of from 1% to 10% by volume.

10 62. The chemical-mechanical polishing process of claim 55 wherein the solution comprises a surfactant selected from group consisting of polyethylene glycol, polyoxyethylene ether, glycerol, polypropylene glycol, polyoxyethylene lauryl ether, polyoxyethylene cetyl ether, polyoxyethylene stearyl ether, polyoxyethylene oleyl ether, and mixtures thereof.

15 63. The chemical-mechanical polishing process of claim 55 wherein the solution further comprises a thickener and has a viscosity of from about 10 centipoise to 20 centipoise at room temperature.

20 64. The chemical-mechanical polishing process of claim 55 wherein the layer consists essentially of elemental copper.

65. The chemical-mechanical polishing process of claim 55 wherein the layer consists essentially of a copper alloy.

25 66. The chemical-mechanical polishing process of claim 55 wherein the polishing is conducted with a solution which is void of solid abrasive material at least prior to starting said polishing.

30 67. The chemical-mechanical polishing process of claim 55 wherein the solution further comprises a copper corrosion inhibitor.

68. The chemical-mechanical polishing process of claim 67 wherein the inhibitor is selected from the group consisting of benzotriazole, mercaptabenzothiazole, tolytriazole, methylamine, diethylamine, pyridine, quinoline, 35 dicyclohexamine nitrate, potassium silicate, ammonium borate, ammonium phosphate, potassium dichromate and mixtures thereof.

69. The chemical-mechanical polishing process of claim 55 comprising maintaining temperature of the solution during polishing at or below about 74°F.

70. The chemical-mechanical polishing process of claim 55 comprising
5 maintaining temperature of the solution during polishing at or below about 65°F.

71. The chemical-mechanical polishing process of claim 55 further comprising chemical-mechanical polishing another of said semiconductor wafer in another polishing step using the fixed abrasive pad, the fixed abrasive pad
10 comprising an elongated web of fixed abrasive pad material having a length greater than a maximum diameter of the said wafers being polished, the process comprising moving the web a distance less than the maximum diameter to polish the another wafer with a fresh pad segment not utilized to polish the first polished wafer.

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72. The chemical-mechanical polishing process of claim 71 wherein the distance is less than or equal to 1.0% of the maximum diameter.

73. A copper layer chemical-mechanical polishing solution specifically
20 adapted for chemical-mechanical polishing with a fixed abrasive pad, the solution comprising a copper oxidizing component present at from about 0.1% to 15% by volume, a copper complexing agent present at from about 0.1% to 15% by volume, and a pH of greater than or equal to 7.0.

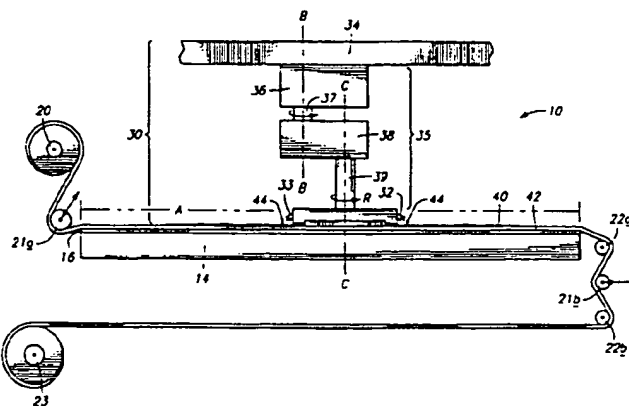
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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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| (74) Agent: MATKIN, Mark, S.; Suite 1300, West 601 First Avenue, Spokane, WA 99201-3828 (US). | | | |
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(54) Title: **COPPER CHEMICAL-MECHANICAL POLISHING PROCESS USING A FIXED ABRASIVE POLISHING PAD AND A COPPER LAYER CHEMICAL-MECHANICAL POLISHING SOLUTION SPECIFICALLY ADAPTED FOR CHEMICAL-MECHANICAL POLISHING WITH A FIXED ABRASIVE PAD**



(57) Abstract

The invention comprises copper chemical-mechanical polishing processes using fixed abrasive polishing pads, and copper layer chemical-mechanical polishing solutions specifically adapted for chemical-mechanical polishing with fixed abrasive pads. In one implementation, processes are described for pH's of 7.0 or greater. In one implementation, processes are described for pH's of 7.0 or less. In one implementation, a copper layer chemical-mechanical polishing solution specifically adapted for chemical-mechanical polishing with a fixed abrasive pad comprises a copper oxidizing component present at from about 1 % to 15 % by volume, a copper corrosion inhibitor present at from about 0.01 % to 2 % by weight, and a pH of less than or equal to 7.0. In one implementation, a copper layer chemical-mechanical polishing solution specifically adapted for chemical-mechanical polishing with a fixed abrasive pad comprises a copper oxidizing component present at from about 0.1 % to 15 % by volume, a copper complexing agent present at from about 0.1 % to 15 % by volume, and a pH of greater than or equal to 7.0.

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INTERNATIONAL SEARCH REPORT

International Application No.

PCT/US 99/27034

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 H01L21/321 C09G1/02 C09K3/14

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 H01L C09G C09K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

WPI Data, INSPEC, PAJ, EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category * | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|------------|--|--|
| X | WO 98 18159 A (MICRON TECHNOLOGY) 30 April 1998 (1998-04-30) page 8, line 3 - line 14 | 1,2,6-8, 15, 20-22, 26,28,33 |
| Y | | 1-73 |
| X | WO 98 49723 A (MINNESOTA MINING AND MANUFACTURING) 5 November 1998 (1998-11-05) abstract page 20, line 21 -page 24; claim 8 -/- | 34-37, 39-42, 46, 48-51, 55-60, 64, 66-69,73 |

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|------------|--|---|
| Y | EP 0 846 742 A (CABOT CORP) 10 June 1998 (1998-06-10) claims | 1-33 |
| A | EP 0 747 939 A (TOSHIBA) 11 December 1996 (1996-12-11) abstract | 1-33 |
| Y | EP 0 659 858 A (TOSHIBA) 28 June 1995 (1995-06-28) claims | 34-73 |
| P,X | EP 0 913 442 A (HITACHI) 6 May 1999 (1999-05-06) claims | 1,2,6-9, 11,12, 20-23, 25,26, 33-35, 38,46, 48-51, 55-57, 64, 66-69,73 |
| A | LUO Q ET AL: "Chemical-mechanical polishing of copper in alkaline media" THIN SOLID FILMS,CH,ELSEVIER-SEQUOIA S.A. LAUSANNE, vol. 311, no. 1-2, 31 December 1997 (1997-12-31), pages 177-182, XP004121339 ISSN: 0040-6090 page 181, right-hand column, last paragraph | 34-73 |

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 99/27034

Box I Observations where certain claims were found unsearchable (Continuation of Item 1 of first sheet)

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because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
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3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of Item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

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2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
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FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. Claims: 1-33

A process for polishing a copper-containing layer using a fixed abrasive pad and a solution at pH lower than 7.0 of an oxidizing component and a copper corrosion inhibitor; polishing solution therefor.

2. Claims: 34-73

A process for polishing a copper containing layer using a fixed abrasive pad and a solution at pH higher than 7.0 of an oxidizing component and a copper complexing agent; polishing solution therefor.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 99/27034

| Patent document cited in search report | Publication date | Patent family member(s) | Publication date |
|---|---------------------|---|--|
| WO 9818159 A | 30-04-1998 | US 5972792 A AU 5148198 A EP 0946979 A | 26-10-1999 15-05-1998 06-10-1999 |
| WO 9849723 A | 05-11-1998 | AU 7170698 A | 24-11-1998 |
| EP 846742 A | 10-06-1998 | US 5954997 A AU 5373998 A JP 11021546 A WO 9826025 A | 21-09-1999 03-07-1998 26-01-1999 18-06-1998 |
| EP 747939 A | 11-12-1996 | JP 9055363 A US 6046110 A | 25-02-1997 04-04-2000 |
| EP 659858 A | 28-06-1995 | JP 7233485 A KR 165145 B US 5575885 A | 05-09-1995 15-01-1999 19-11-1996 |
| EP 913442 A | 06-05-1999 | JP 11135466 A CN 1216727 A | 21-05-1999 19-05-1999 |

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